Mössbauer Effect in SnI (Special Issue on Physical, Chemical and Biological Effect of Gamma Radiation, XIV)

AUTHOR(S):

Katano, Rintaro; Mukoyama, Takeshi

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 51, No. 1, 1973

Mössbauer Effect in SnI_4

Rintaro KATANO and Takeshi MUKOYAMA*

Received January 10, 1973

Mössbauer measurements of the 23.8-keV transition in ^{119}Sn and of the 57.6-keV transition in ^{127}I have been carried out in order to investigate the chemical bond in SnI_4. The isomer shifts for Sn and for I have been obtained. These data combined with the iodine NQR data of the quadrupole splitting have been used to interpretate the bond structure. The Sn–I bond in SnI_4 contains about 23 % π-character, and 5 % s-hybridization is presented in the iodine σ-orbital. These results are in good agreement with the previous interpretation of the Mössbauer experiments for ^{119}Sn and ^{129}I. The effective charge on the iodine atom is $-0.022e$ and that on the tin atom is $+0.088e$.

I. INTRODUCTION

The technique of resonance absorption of recoil-free γ rays (Mössbauer effect) has been extensively applied to the study of the electronic structure of various chemical compounds. The parameters obtained from this method, isomer shift, nuclear quadrupole coupling constant, and asymmetry parameter, have been shown to be related to the molecular structure and the nature of chemical bond. It is one of the most interesting subjects to study these parameters for a molecular crystal containing only two kinds of atoms, both of which can be studied by resonance absorption technique. Stannic iodide, SnI_4, is such a molecule and is the most suitable for this purpose because of its simple crystal structure.

In stannic iodide molecule, the iodine atoms at the corner of a tetrahedron are covalently bound to the tin atom in the center. The intermolecular bonding is made mainly by van der Waals forces.[1] Therefore, intermolecular influence on the charge density and distribution at the atomic nucleus is negligible. The crystal structure is cubic. Three of the iodine sites are equivalent but the fourth is an inequivalent one. Since the iodine atom is located on one of the C_{3V} axes of the molecule, there exists an axially symmetric electric field at the iodine-atom site but not at the tin-atom site.

Mössbauer experiments for tin have been reported using the recoil-free γ radiation from the first excited state of the ^{119m}Sn (23.8 keV). On the other hand, there are two isotopes of iodine suitable for Mössbauer experiments; ^{127}I and ^{129}I. The former is stable with 100 % natural abundance, while the latter is radioactive with a half-life of 1.7×10^7 years. The isotope ^{127}I has a 57.6-keV transition from the first excited state of spin $7^+/2$ to the ground state $5^+/2$. The source is the 109-day ^{127m}Te which feeds the 57.6-keV state by various ways. On the other hand, the isotope ^{129}I has a 27.8-keV γ radiation emitted in the transition between states of the same spin and parity as ^{127}I, but the order of the levels is inverted. The source is ^{129m}Te with a half-life of 34 days.

* 片野林太郎, 向山　毅: Laboratory of Nuclear Radiation, Institute for Chemical Research, Kyoto University, Kyoto.

This state decays predominantly to the 27.8-keV level of ^{129}I through the ground state of ^{129}Te.

Since the line width of resonance absorption obtained with ^{129}I is narrower than that with ^{127}I, a well resolved spectrum can be observed for ^{129}I, while levels split by quadrupole interaction are only partially resolved in the case of ^{127}I. This fact indicates that ^{129}I is superior for chemical studies, but the difficulty in the chemical preparation of the absorber overrides this advantage.

For the compound SnI_4, there were a number of Mössbauer studies using the ^{119m}Sn source. However, no more than one Mössbauer experiment has been performed on the iodine in SnI_4. Bukshpan and Herber[2] have observed recoilless resonance absorption for ^{119}Sn and ^{129}I in SnI_4. They analyzed the ^{129}I Mössbauer data and derived the information about the Sn–I bond. Under the assumption that only p-electrons of the iodine atom contribute to the bonding, they concluded that the Sn–I bond in SnI_4 has principally a σ-character with a small π-electron interaction.

On the other hand, Gordanskii *et al.*[3] have derived expressions relating isomer shifts in tin tetrahalides with the electronic structure of tin. Using the reported value of the isomer shift for tin and the result of nuclear quadrupole resonance (NQR) measurement on iodine in SnI_4, they indicated that the π interactions in SnI_4 is of the same order of magnitude as the σ interactions.

To resolve this discrepancy, Ehrlich and Kaplan[4] have analyzed the Mössbauer data for both ^{119}Sn and ^{129}I. By including a small s-hybridization in the iodine bond, the ^{129}I Mössbauer data of Bukshpan and Herber were reanalyzed and could be explained to yield a consistent interpretation of the chemical bond in SnI_4. They concluded that the Sn–I bond contains about 23 % π-character and 5–6 % s-hybridization is involved in the iodine σ-orbital.

It is worthwhile to study the Sn–I bond in SnI_4 by observing the Mössbauer effect for another iodine isotope, ^{127}I. In the present work, the chemical bond in SnI_4 was investigated by a Mössbauer experiment for the same SnI_4 absorber using the 23.8-keV γ radiation in ^{119}Sn and the 57.6-keV transition in ^{127}I. Because of poor resolution of the ^{127}I spectrum, the quadrupole coupling constant obtained by the NQR method was used to analyze the experimental spectrum. Combining the isomer shift obtained and the NQR data and following the treatments of Ehrlich and Kaplan,[4] a consistent interpretation of the chemical bond in SnI_4 was made.

II. EXPERIMENTAL

The measurements of resonance absorption spectra for SnI_4 were performed with two isotopes, ^{119}Sn and ^{127}I. For the Sn experiment, a 5-mCi $Ba^{119m}SnO_3$ source purchased from New England Nuclear Corporation was used. In the I work, we prepared our own source of $Zn^{127m}Te$ from the 4N HCl solution of $H_2{}^{127m}TeO_3$. The nonradioactive compound of ZnTe was prepared by heating a mixture of natural metallic zinc and tellurium, 1 : 2 by weight, at 1100°C in an evacuated quartz ampoule. The The structure of this compound was examined by X-ray diffraction analysis. Then the product was powdered. After radioactive solution of ^{127m}Te was added, the sample was heated again at 1100°C in the evacuated quartz tube. This tube was used as a

source capsule. The absorber of a thickness of 30 mg/cm^2 was sealed into a lucite holder.

The measurements were carried out in a Dewar at liquid-nitrogen temperature for Sn and at liquid-helium temperature for I. Both source and absorber were immersed into the liquid and were held at these temperatures. The Mössbauer drive used in these experiments has been described elsewhere.[5] It consists of an electromechanical drive unit coupled to a long vertical drive rod by a double-bellow assembly. The apparatus is placed vertically into a Dewar. The absorber is moved sinusoidally by a mechanical linkage.

The 57.6-keV γ rays of ^{127}I and the 23.8-keV γ rays of ^{119}Sn were detected by a 1-mm-thick NaI(Tl) detector mounted on a Toshiba 7696 photomultiplier.

The velocity was calibrated with a standard ^{57}Co source in copper and an enriched metallic iron absorber.[6]

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Experiment for Sn

In the quadrivalent tin compounds such as SnI_4, the tin atom occupies the center of a tetrahedron formed by four identical atoms. Therefore, the electric field gradient at the tin nucleus must be very small or zero and the singlet spectrum is expected.

The resonance absorption experiment for Sn was performed with both the source and absorber cooled by liquid nitrogen. The Mössbauer spectrum observed for SnI_4 is

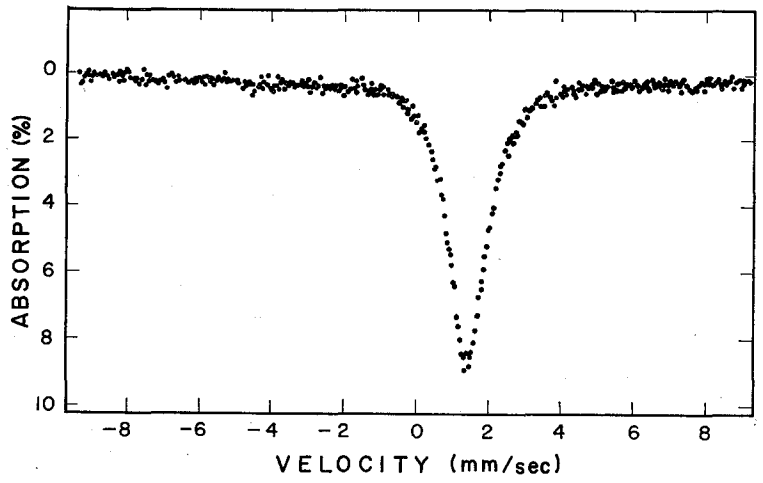

Fig. 1. Mössbauer spectrum at 77°K of a SnI_4 absorber and a $Ba^{119m}SnO_3$ source.

shown in Fig. 1. The value of the isomer shift obtained from the spectrum is +1.55 mm/sec with respect to $BaSnO_3$. This result agrees well with the values reported in the literature.[7]

The isomer shift of tin is sensitive to changes in the 5s electron density at the nucleus. A neutral tin atom has an electron configuration of $4d^{10}5s^25p^2$ outside the krypton core, while completely ionic stannic compounds have the configuration $4d^{10}$.

The covalent compounds have an intermediate number $5s$ and $5p$ electrons depending on the nature of the hybridization and on the partial ionic character of the chemical bond. For the tetravalent tin compounds, there is a correlation between the isomer shift and the electronegativity difference of the component atoms.[8] The ionic character of the bond, which is closely correlated to the electronegativity difference, can be estimated from the isomer shift. From the value of the isomer shift and the small value of the difference in electronegativity between tin and iodine, the chemical bond in SnI_4 is found to be essentially covalent. The structure studies by X rays indicate that SnI_4 is tetrahedral with four equivalent sp^3-hybrid orbitals.

For the isomer shift of tin tetrahalides, Godanskii *et al.*[3] have obtained the expressions relating isomer shifts with the electronic structure of tin. Making use of their result and neglecting the contributions from d-orbitals to the bonding, the isomer shift δ (mm/sec) with respect to α-tin can be written as

$$\delta=7.5\{[1+0.17(3-P-P_\pi)]^2-0.17\}S-6.23, \tag{1}$$

where P is the population of valence $p\sigma$-orbitals, P_π is that of valence $p\pi$-orbitals, and S is that of valence s-orbitals. According to Goldanskii *et al.*,[3] it can be assumed for all tin tetrahalides that

$$3-P-P_\pi\simeq 0. \tag{2}$$

Combining our isomer shift data for SnI_4 with respect to $BaSnO_3$ and the value of isomer shift for α-Sn with respect to $BaSnO_3$ at 80°K, +2.10 mm/sec,[9] the isomer shift for SnI_4 with respect to α-Sn was determined to be

$$\delta=-0.55 \text{ mm/sec}. \tag{3}$$

Substituting this value into Eq. (1) and making use of Eq. (2), we obtain the value for the population of $5s$ states of tin in stannic iodide:

$$S=0.91. \tag{4}$$

B. Experiment for I

At the I site of SnI_4 exists an axially symmetric electric field gradient. A quadrupole splitting of the Mössbauer spectrum is, therefore, expected for the ^{127}I experiment. When the asymmetry parameter η is zero, the line positions (mm/sec) of the quadrupole splitting is represented as[10]

$$\delta_{ij}=\frac{ce^2qQ}{4E_\gamma}\left[\frac{Q^*}{Q}C(I^*, m_j)-C(I, m_i)\right]+\delta, \tag{5}$$

where E_γ is the energy of γ rays, I is the spin of the ground state, m_i is the quantum number of I_z, Q is the quadrupole moment of the ground state of the iodine nucleus in SnI_4, the asterisk stands for the excited state of the nucleus, e^2qQ is the quadrupole coupling constant of SnI_4, δ is the isomer shift for ^{127}I in SnI_4 with respect to the ZnTe source, and

$$C(I, m)=[3m^2-I(I+1)]/I(2I-1).$$

Since the excited state has a spin $I^*=7/2$ and the ground state $I=5/2$ and the multipolarity of the transition between them is pure Ml, combinations of m_i and m_j

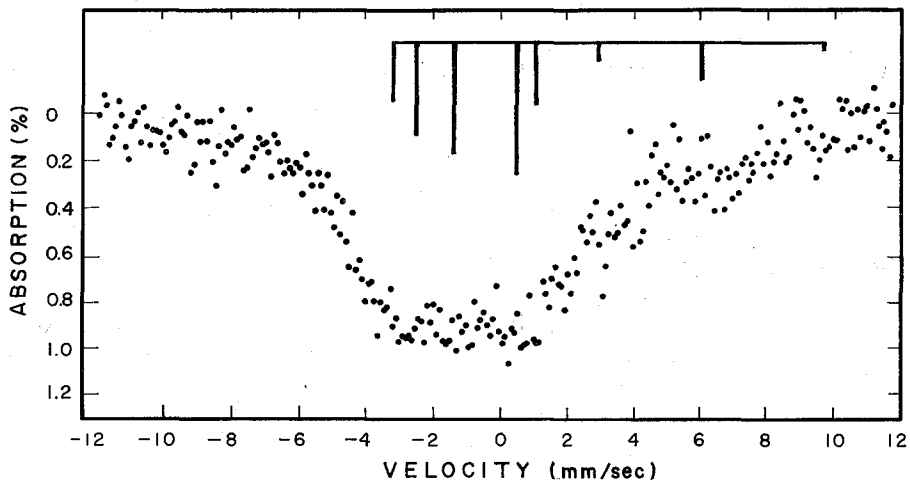

Fig. 2. Mössbauer spectrum at 4.2°K of a SnI_4 absorber and a $Zn^{127m}Te$ source. The vertical lines indicate the computed peak positions and relative intensities resulting from the quadrupole interaction.

($m_i - m_j = 0, \pm 1$) give an eight-line splitting spectrum. The spectrum obtained with the single-line $Zn^{127m}Te$ source at liquid-helium temperature is shown in Fig. 2. Because resolution of the ^{127}I spectrum is poor, the spectrum is not well resolved. Therefore we decided to use the available NQR data for SnI_4 to analyze the experimental spectrum.

The ratio Q^*/Q, independent of the chemical structure of the iodine compounds, has been determined to be 0.896 ± 0.002 by Perlow and Ruby.[11] For the quadrupole coupling of the ground state in SnI_4, we used the value of $e^2qQ = -1384$ MHz measured by Schawlow using the NQR method.[12] Using these values, the experimental spectrum in Fig. 2 was analyzed by the method of least-squares with a FACOM 230-60 computer in the Data Processing Center of Kyoto University. The hyperfine components were assumed to be Lorentzian with relative peak intensities calculated from the Clebsch-Gordan coefficients. The isomer shift thus determined is

$$\delta = -0.18 \pm 0.05 \text{ mm/sec}, \tag{6}$$

with respect to ZnTe. This value is in good agreement with the value estimated from the ^{129}I isomer shift by multiplying with a conversion factor of -0.35.[13]

According to the theory of Townes and Dailey, the molecular quadrupole coupling constant of the iodine atom in SnI_4, e^2qQ, is related to that of a free iodine atom, $e^2q_{at}Q$, by[14]

$$e^2qQ = -U_p e^2 q_{at} Q, \tag{7}$$

where U_p is the difference between the p-electron population in the z direction and that in the x and y directions. If U_x, U_y, and U_z represent the electron populations of $5p_x$, $5p_y$, and $5p_z$ states of the iodine atom, U_p can be expressed as

$$U_p = U_z - \frac{1}{2}(U_x + U_y). \tag{8}$$

To the first approximation, Eq. (7) can be written by[3]

$$-\frac{e^2q_{at}Q}{e^2qQ}=\frac{1}{4}B(S+P)-\frac{1}{8}P_\pi, \tag{9}$$

where B is the fractional p-character in the iodine σ-orbital involved in a bond with Sn, S, P, and P_π are the same as those defined in Eq. (1). In the first term of Eq. (9), the sum $(S+P)$ corresponds to the number of electrons in the σ-orbitals. Using the value obtained by the NQR experiment $e^2qQ=-1384$ MHz[12] and $e^2q_{at}Q=2293$ MHz,[15] it is shown that

$$\frac{1}{4}B(S+P)-\frac{1}{8}P_\pi=0.604. \tag{10}$$

In the iodine atom, the removal of a valence s-electron diminishes the iodine isomer shift, while the removal of p-electron increases it by reducing the shielding effect on the s-electrons. Taking into account these effects, Perlow and Perlow[16] derived the formula for the isomer shift for ^{127}I:

$$\delta=K[-h_s+\gamma(h_s+h_p)(2-h_s)], \tag{11}$$

where δ is the ^{127}I isomer shift with respect to I^-, h_s and h_p are the numbers of the s- and p-electron holes in the valuence shell of the closed atom I^- ($5s^25p^6$), and $2K\gamma$ is the isomer shift per p-electron hole.

The value of the shielding constant γ has been estimated by Wilson[17] to be 0.07 in the neighborhood of the closed shell using the Hartree-Fock calculations. Perlow and Perlow[16] have plotted h_p of the various iodine compounds determined from quadrupole couplings against the isomer shifts and obtained the value of the shift per $5p$-electron hole in the iodine:

$$2K\gamma=-0.56 \text{ mm/sec.}$$

Inserting these numerical values and using our isomer shift data for SnI_4 and the deduced value for the isomer shift for I^- of 0.164 mm/sec,[16] we get:

$$-0.34=-3.57[-h_s+0.07(h_p+h_s)(2-h_s)]. \tag{12}$$

The parameters, h_s and h_p, can be expressed using B, S, P, and P_π. Since $(1-B)$ represents the fractional s-character in the σ-orbital, h_s is written by

$$h_s=\frac{1}{4}(1-B)(S+P), \tag{13}$$

and also

$$h_p=\frac{1}{4}B(S+P)+\frac{1}{4}P_\pi. \tag{14}$$

Adding Eqs. (13) and (14) and using Eqs. (2) and (4) we find:

$$h_s+h_p=\frac{1}{4}(S+P+P_\pi)=0.978. \tag{15}$$

From Eqs. (12) and (15), the population of s-electron hole in the I^- atom is

$$h_s=0.039, \tag{16}$$

and from Eq. (15)

$$h_p=0.939. \tag{17}$$

The population of $5p$-orbitals in SnI_4 and the fractional p-character of the σ-orbital are obtained by making use of Eqs. (2), (4), (10), and (14):

$$P=2.11, \quad P_\pi=0.89, \quad B=0.95. \tag{18}$$

IV. CONCLUSION

From the results presented above, π-character of the Sn–I bond is calculated by

$$\Pi=\frac{P_\pi}{S+P+P_\pi}=0.23. \tag{19}$$

This result indicates that the Sn–I bond in SnI_4 has 23 % π-character. From the value of B, s-hybridization in the σ-orbital in the iodine atom is 5 %. These results obtained are in good agreement with the results of Goldanskii *et al.*[3] and the interpretation of Ehrlich and Kaplan,[4] but inconsistent with the interpretation of the ^{129}I experiment by Bukshpan and Herber.[2] This discrepancy comes from the assumption made by them, that the Sn–I bond is primarily made by p-electrons.

From Eq. (15), it can be seen that both iodine and tin atoms are essentially neutral and the net charges on the iodine atom is -0.022 and on the tin atom $+0.088$.

Although resolution of the measurement is poor, the Mössbauer effect of the 57.6-keV transition in ^{127}I can provide useful information about the iodine bond when its result is combined with data obtained from the other method such as NQR. It is interesting to study in this method the chemical bond of GeI_4. This is also an iodine compound, both of its component atoms can be studied by the Mössbauer effect.

ACKNOWLEDGMENT

The authors wish to express their thanks to Professor S. Shimizu for his encouragement.

REFERENCES

(1) R. W. Lynch and H. G. Drickamer, *J. Chem. Phys.*, **45**, 1020 (1966).
(2) S. Bukshpan and R. H. Herber, *J. Chem. Phys.*, **46**, 3375 (1967).
(3) V. I. Goldanskii, E. F. Makarov, and R. A. Stukan, *J. Chem. Phys.*, **47**, 4048 (1967).
(4) B. S. Ehrlich and M. Kaplan, *Chem. Phys. Letters*, **3**, 161 (1969).
(5) R. Katano, *Nucl. Instr. and Meth.*, **83**, 187 (1970).
(6) R. S. Preston, S. S. Hanna, and J. Heberle, *Phys. Rev.*, **128**, 2207 (1962).
(7) *Mössbauer Effect Data Index, 1970*, J. G. Stevens and V. E. Stevens, ed. (IFI/Plenum Data Corporation, New York, 1972).
(8) R. I. Gol'danskii, G. M. Gorodinskii, L. A. Korytko, L. M. Krizhanskii, E. F. Makarov, I. P. Suzdalev, and V. V. Khrapov, *Proc. Dubna Conf. Mössbauer Effect* (Consultants Bureau Enterprises, Inc., New York, 1963).
(9) J. D. Donaldson and D. G. Nicholson, *J. Chem. Soc.*, **A1970**, 145 (1970).
(10) D. W. Hafemeister, in *An Introduction to Mössbauer Spectroscopy*, L. May, ed. (Plenum Press Inc., New York, 1971), p. 58.
(11) G. J. Perlow and S. L. Ruby, *Phys. Letters*, **13**, 198 (1964).
(12) A. L. Schawlow, *J. Chem. Phys.*, **22**, 1211 (1954).

(13) K. R. Reddy, F. De S. Barros and S. DeBenedetti, *Phys. Letters*, **20**, 297 (1966).
(14) T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy* (Academic Press Inc., New York, 1958).
(15) V. Jaccarino, J. G. King, R. A. Satten, and H. H. Stroke, *Phys. Rev.*, **94**, 1798 (1954).
(16) G. L. Perlow and M. R. Perlow, *J. Chem. Phys.*, **45**, 2193 (1966).
(17) M. Wilson, *Phys. Rev.*, **176**, 58 (1968).